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A Comparative Second Harmonic Study of Cu(111) in UHV and in
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by

R. Bradley, A. Friedrich, E. K. L. Wong and G. L. Richmond

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Department of Chemistry
University of Oregon
Eugene, OR 97403

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<p>This paper provides important new information about the surface properties of a copper single crystal electrode as examined by surface optical second harmonic (SH) generation. The unique aspect of the work is that SH response from the Cu(111) electrode surface was examined and compared with identical studies performed on this surface in ultra-high vacuum. The results provide compelling evidence for the existence of surface oxides even under conditions where one might expect the electrode surface to be oxide free.</p>					
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A Comparative Second Harmonic Study of Cu(111) in UHV and in Solution

R.A. Bradley, K.A. Friedrich, E.K.L. Wong and G.L. Richmond

**Chemical Physics Institute, University of Oregon,
Eugene, Oregon 97403**

Introduction

Recent studies from this laboratory have shown that experiments involving the rotational anisotropy in the surface second harmonic (SH) response from single crystal metal surfaces can provide important information about the electronic and atomic structure of these surfaces [1,2]. The unique aspect of this nonlinear optical technique is its experimental simplicity, its adaptability to examining a variety of buried interfaces in-situ, and its surface specificity. For electrochemical applications, the ability to make comparative measurements on a surface in a variety of environments including in the electrochemical cell, under ambient conditions and under ultra-high vacuum (UHV) conditions, offers enormous potential for tying together numerous previous studies which could only be performed in a single environment.

This paper demonstrates the importance of being able to make such comparative measurements and provides insight into the surface properties of a Cu(111) surface in an electrolyte solution. In these experiments the SH response from a Cu(111) surface is measured in an electrochemical environment under potentiostatic control, in UHV and in the presence of oxygen. In previous related SH studies performed on Ag(111), the surface was found to have similar structural and electronic properties when the experiments were conducted in UHV and in the electrochemical cell at the PZC [2,3,4]. In contrast, we find the Cu(111) surface properties in solution are very different than what one observes at the surface/vacuum interface. Further, we provide evidence for the existence of oxygen containing surface species which appear to be a major factor for

this difference and whose presence should play a role in any simple electrochemical processes examined on a copper surface.

Theory

The unique sensitivity of SHG to the interfacial region arises from the fact that in the dipole approximation, this nonlinear process is forbidden in the bulk of centrosymmetric media. At an interface such as the electrode/electrolyte junction, the bulk inversion symmetry is broken and therefore second harmonic generation is allowed. In the dipole approximation SHG is described by the induced polarization of second order [5]:

$$P^{(2)}(2\omega) = \chi^{(2)} : E(\omega) E(\omega) \quad (1)$$

where the susceptibility $\chi^{(2)}$ is a tensor of third rank describing all second order optical properties and the symmetry of the medium. In general, a (111) surface has C_{3v} symmetry when two or more atomic layers are considered. With p-polarized excitation, it has been shown that the p-polarized SH response from this 3-fold symmetric surface yields the following angular dependence upon azimuthal rotation [6]:

$$I(2\omega)^{p/p} \sim (a^{(\infty)} + c^{(3)} \cos(3\phi))^2 \quad (2)$$

where $a^{(\infty)}$ and $c^{(3)}$ are referred to as the isotropic and anisotropic coefficients, respectively. For metals, both coefficients are complex and are comprised of susceptibility tensor elements and corresponding fresnel factors at ω and 2ω . The tensor elements incorporated into the coefficient $a^{(\infty)}$ represent the out-of-plane response (perpendicular to the surface) whereas $c^{(3)}$ contains the surface tensor element responsible for the in-plane polarization. By fitting the data to equation (2), one can

verify the symmetry and obtain the ratio $c^{(3)}/a^{(\infty)}$. This ratio contains a magnitude and phase angle representing the interference between the anisotropic and isotropic susceptibilities (the phase angle is the *difference in the phase*). Furthermore, the ratio provides insight into the electronic properties of the surface (as manifested in the optical response) and into how these properties are altered by some external perturbation [2,4].

Experimental

A conventional optical geometry was used and the details were previously published [7]. The excitation source was a 10 Hz Nd-YAG laser emitting 13 ns light pulses at 1064 nm. An incident angle of 31° for the solution experiment and 45° for the UHV measurements was used. Laser powers of under 3 mJ/pulse were employed to avoid damage to the surface. The orientation of the 99.999 % Cu(111) crystal was determined by Laue back-reflection to be within 1 degree.

For the electrochemical experiments, the crystal was mounted on a rotatable shaft within the electrochemical cell. The azimuthal angle (ϕ) of rotation of the shaft and the crystal is defined as the angle between the $[2\bar{1}\bar{1}]$ direction and the projection of the incident wavevector parallel to the surface. A three electrode geometry was used with all potentials reported relative to the Ag/AgCl reference electrode. Crystal preparation and all electrochemical procedures including sample mounting were performed under an inert atmosphere. The solutions were continuously purged with oxygen free nitrogen throughout the course of the experiments. The standard electropolishing method for copper was used which has been described previously [8].

The vacuum experiments were performed in a chamber with a base pressure of 3.5×10^{-10} torr and the crystal was cleaned by sputtering and annealing procedures. Auger and LEED were used to check the cleanliness and order of the sample.

Results and Discussion

Figure 1 shows the rotational anisotropy of Cu(111) in 0.01 M HClO₄ at pH 2 at -0.2 V vs. Ag/AgCl, which is near the potential of zero charge (PZC) [9]. The data has been fit with the equation (2). The ratio of the phenomenological constants $c^{(3)}/a^{(\infty)}$ obtained by the fit gives a value of $0.9(\pm 0.1) e^{i125^\circ}$. The SH anisotropy pattern from Cu(111) shows very little variation as the potential is scanned between the limits of the double layer charging region of -0.1 V to -0.4 V vs Ag/AgCl. The present solution results are slightly different from those of a previously published rotational anisotropy study of Cu(111) [12]. We will discuss the detailed differences in a future publication [13].

Under these electrolytic conditions and a potential bias near the PZC, one might expect to have a surface which is least perturbed by the electrochemical double layer and thus would give the closest representation of the SH response obtained from this surface in UHV. This was proven to be true for Ag(111), for which nearly identical optical parameters were found for the surface biased at the PZC and for the surface measured in UHV [3].

Figure 2 displays the SH rotational anisotropy obtained from this crystal examined under UHV conditions. Of significance is the surprisingly different SH pattern obtained from the surface in vacuum relative to the surface in solution (Fig. 1). This difference is manifested in the change of the ratio $c^{(3)}/a^{(\infty)}$, which in UHV is equal to $1.2(\pm 0.1) e^{i77^\circ}$. Not only is there a change in the magnitude of the ratio (0.9 vs. 1.2), but more importantly there is a distinct difference in the phase angle .

The fact that both scans (Fig. 1 and 2) can easily be fit to the expression in equation (2) suggests that both have a 3-fold symmetric surface and that this interfacial symmetry is not perturbed by the presence of the electrolyte or possible adsorbates. However, the rather large changes in the magnitude and phase angle of the rotational anisotropies suggests that the surface electronic properties in solution are very different

than in UHV. The difference in angle of incidence for the two experiments cannot account for this observation. Since at the PZC the effect of the DC electric field should be minimal, these differences in the SH response can not be attributed to the presence of the static field which could cause an additional nonresonant $\chi^{(3)}$ contribution [10], or to a significant potential induced shift in surface electronic states or bands causing resonance effects [2]. Previous experiments performed on Ag(111) under resonant and nonresonant conditions have demonstrated that *at the PZC*, the double layer properties have very little impact on the magnitude or phase angle of the measured anisotropies [2-4]. Therefore we conclude that the different anisotropies from Cu(111) can only be explained by the presence of an adsorbed species which significantly alters the electronic properties of the surface in solution.

One of the most likely adsorbates to cause such a change is oxygen, which by localizing charges in metal-oxygen bonds, can diminish the induced polarization from that of free electrons at a metal surface [14,15]. Previous cyclic voltammetry studies have suggested that oxygen containing species might be present on the surface of copper throughout the double layer charging region, including at the PZC [11]. To check this supposition, we dosed the clean Cu(111) surface in UHV with increasing exposures of oxygen. The resulting oxygen dosed surface gives a SH response which can be more closely correlated to the Cu(111) electrode response than to the clean surface data. As the surface is dosed with O_2 , the initial intensity maximum at $\phi = 0$ progressively decreases to a minimum. As the dosing proceeds, the rotational anisotropy is described by an increasing phase angle. At an exposure of 900 Langmuir of O_2 , it is similar to that obtained in solution. Figure 3 shows the saturated SH response from Cu(111) with 2000 Langmuir of O_2 . When the data is fit to Eq. (2), the value obtained for $c^{(3)}/a^{(\infty)}$ is $0.8(\pm 0.1) e^{i194^\circ}$. This pattern and its fit are also very similar to the angular dependence of SH intensity obtained previously by Tom and Aumiller [16] for Cu(111) under ambient condition. Although we have found that the rotational anisotropy from

Cu(111) in solution shows variations with such parameters as pH and electrolyte, none of these changes can produce a surface response which is the same as that measured for clean Cu(111) in UHV [13]. In our experiment, we can not distinguish the form of the oxygen species which exists at the surface. However, we can conclude from the UHV data that the presence of oxygen, even at low exposures, can cause significant perturbations in the electronic properties of the surface.

In summary, we provide evidence that the Cu(111) surface in solution is very different than what exists in UHV, even under conditions where the effect of the double layer should be minimal. We conclude that these differences in the magnitude and phase angle of the ratio $c^{(3)}/a^{(\infty)}$ are mainly due to Cu-oxygen interactions occurring at the electrode surface. By our observation, the increase in phase angle corresponds to the increase in amount of oxygen present at the surface. The inability to achieve a SH response which is similar to that observed in UHV, even under a variety of electrolytic conditions, calls into question the accuracy of extrapolating structural data derived in UHV to understand the properties of Cu(111) in an electrolytic environment.

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Figure Captions

Figure 1. SH rotational anisotropy from an Cu(111) electrode immersed in 0.01 M HClO₄ at pH 2. P-polarized 1064 nm excitation was used. The electrode potential was held near the PZC, -0.2 V vs Ag/AgCl. The p-polarized SH data is shown with open circles and the theoretical fit using Eq. (2) with solid lines.

Figure 2. SH rotational anisotropy from clean Cu(111) in UHV at 3.5×10^{-10} torr, under p-polarized excitation at 1064 nm. The open circles represent the p-polarized SH data and theoretical fits using Eq.(2) are indicated with a solid line.

Figur 3. SH rotational anisotropy from Cu(111) after exposure to 2000 Langmuir of O₂. Under p-polarized excitation shown are the p-polarized SH data (open circles) and theoretical fits (solid lines) to Eq. (2).

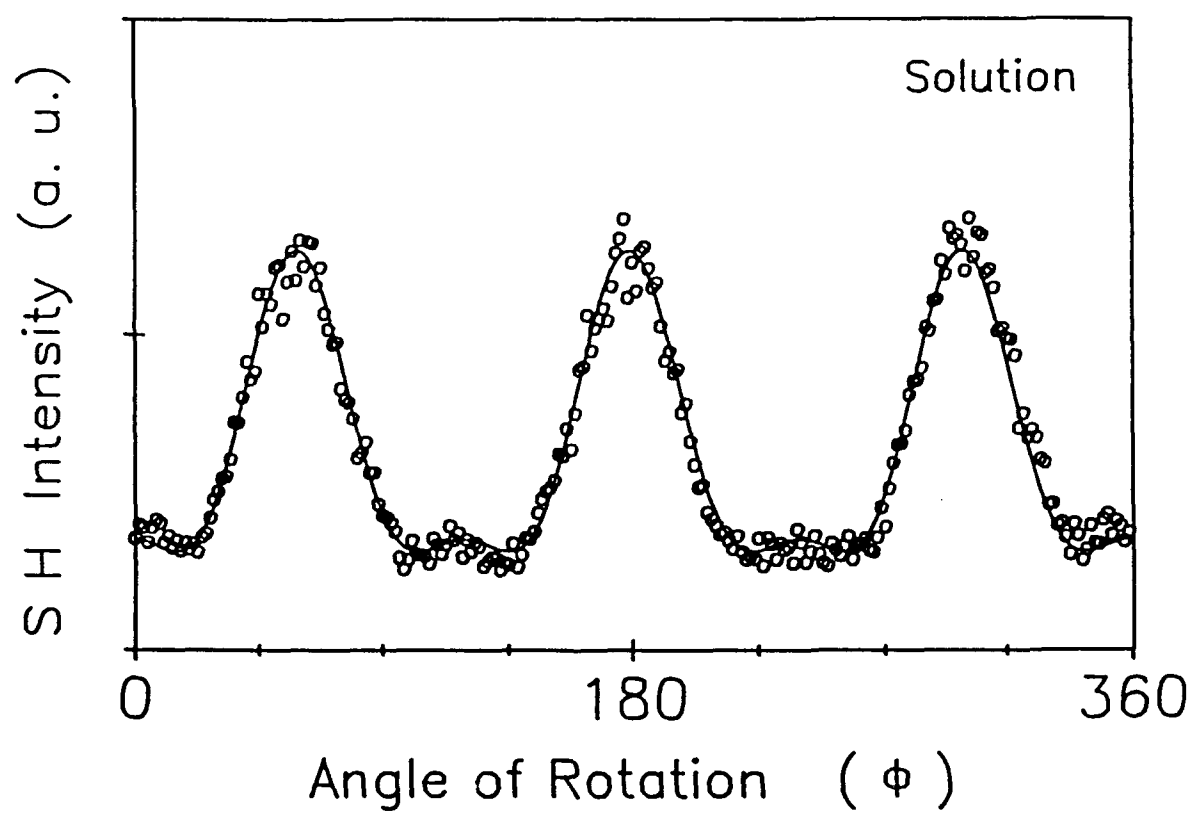
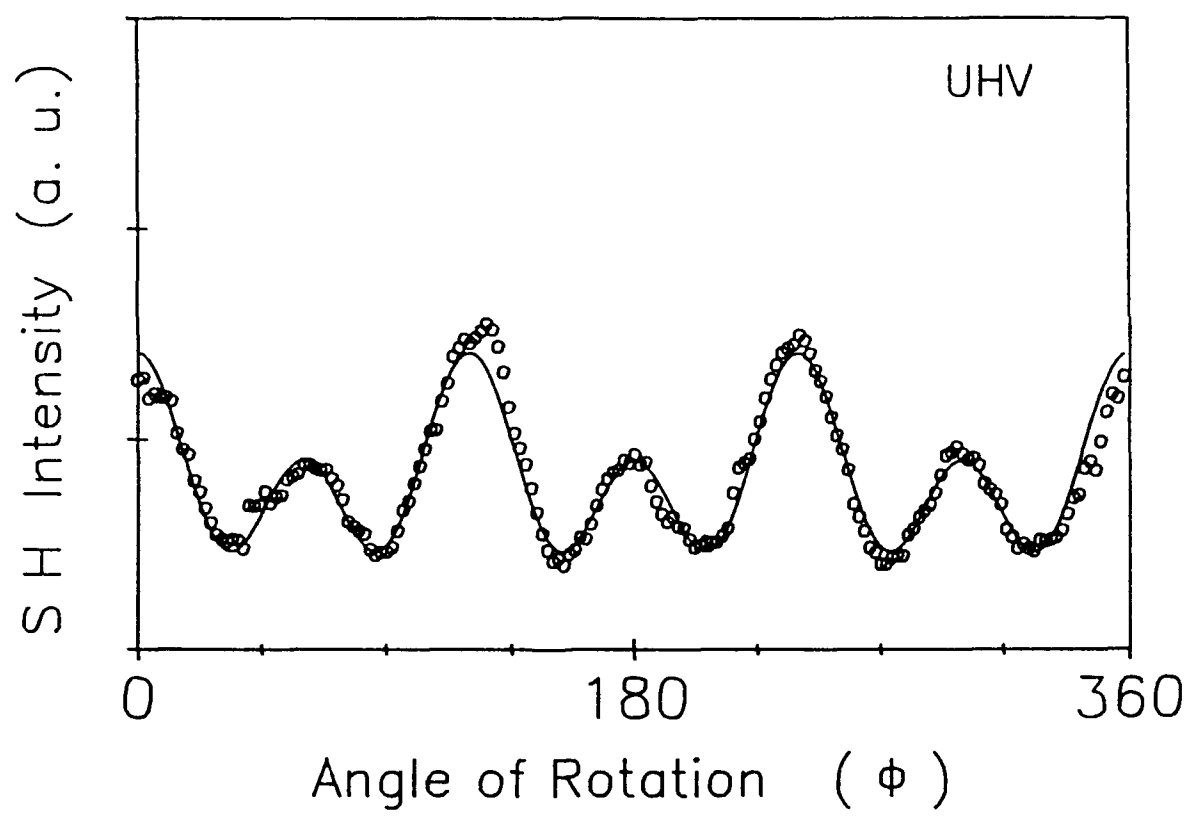


Figure 1



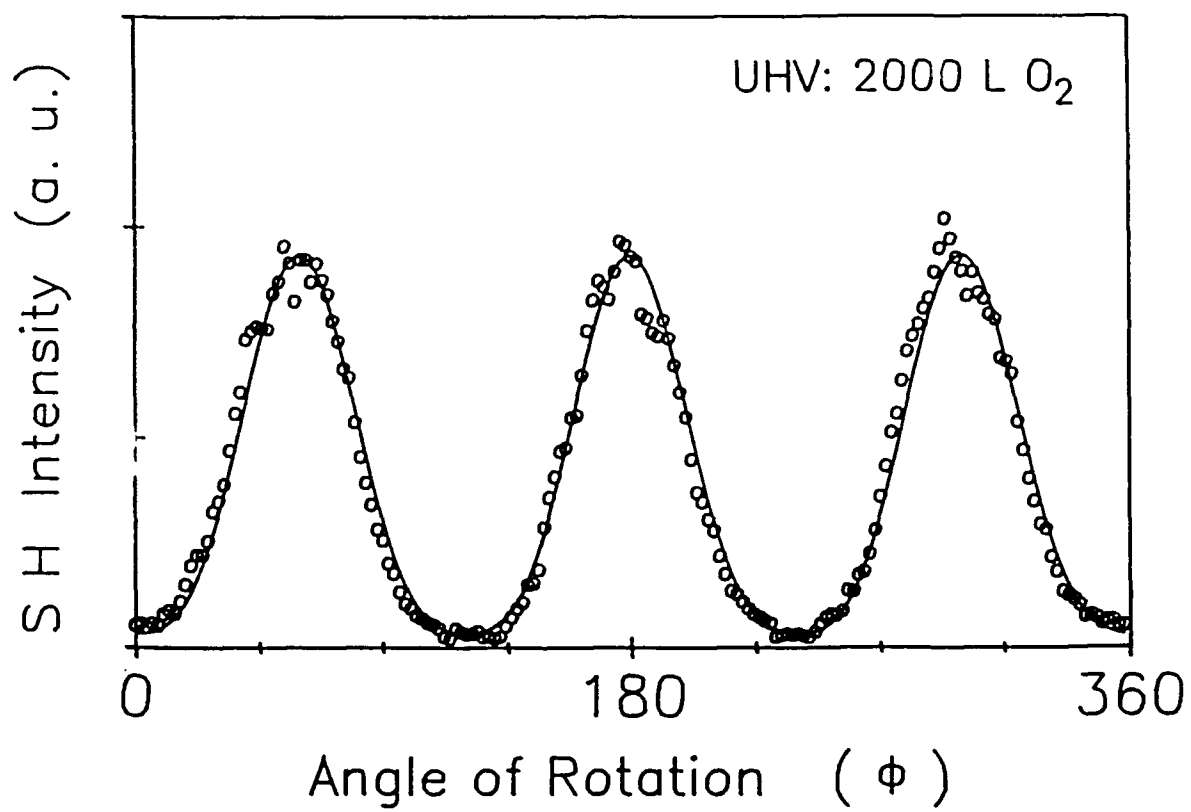


Figure 5